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The Efficiency of Surfactants on Xerographic Ink

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by

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Abstract

Surfactants are used in the deinking process for the dispersion of ink particles, collection of ink particles, and reduction of surface tension. Surfactant characteristics are vital in understanding the efficiency of a surfactant on ink particles. Evaluation on the efficiency of surfactants and on toner particles is critical to optimize a deinking process and improve selection of deinking surfactant candidates.

By deinking xerographic inks with series of nonionic, anionic, and cationic surfactants, the efficiency was reported. By using the HLB (hydrophile-lipophile balance) empirical method of rating surfactants, the efficiency was correlated to structure and other surfactant properties. Normally when the HLB value of a surfactant is high, the hydrophilic nature of the surfactant is high as is the polarity. Also, by contrast, when a surfactant has a low HLB value, it tends to have a higher hydrophobic nature and a more nonpolar characteristic. These values are based on the number of hydrophilic groups on the surfactant primary structure. Thus, by applying these concepts to the process of deinking, this report revealed the efficiency of cationic, anionic, and nonionic surfactants through the results of image analysis and ink removal efficiency.

Overall, the nonionic and cationic surfactants had the best ink removal efficiency. Anionic surfactants showed poor results. For the nonionic and cationic, an increase in ink removal efficiency correlated to a net increase in HLB. An increase in surfactant concentration increased ink removal efficiency for the nonionic and cationic surfactants. Alkaline conditions showed better results for the nonionic than cationic.

Introduction

Xerographic inks are now commonly found in the mainstream of today's office waste. Current deinking processes, which incorporate flotation in their ink removal strategy, have encountered that these inks are very difficult to de-ink due to their particle shape and fused-on-fiber characteristics. These characteristics make ink particles very difficult to remove during flotation alone. The use of surfactants will render ink particles hydrophobic so they can be removed via flotation. However, due to the randomness of ink type in recycled paper, optimization is somewhat limited.

By comparing a specific ink type to a deinking process with varying surfactants, logically, an efficiency rating can be given to that surfactant as to its effect on ink removal. The role of surfactant properties on determining deinking effectiveness is now needed to lead to a better comprehension of the deinking mechanisms and resultant surfactant selection. This experiment correlated the efficiency of cationic, anionic, and nonionic surfactants on xerographic ink particles so that further optimization could be developed.

Theoretical and Background Discussion

Flexographic and Xerographic Inks

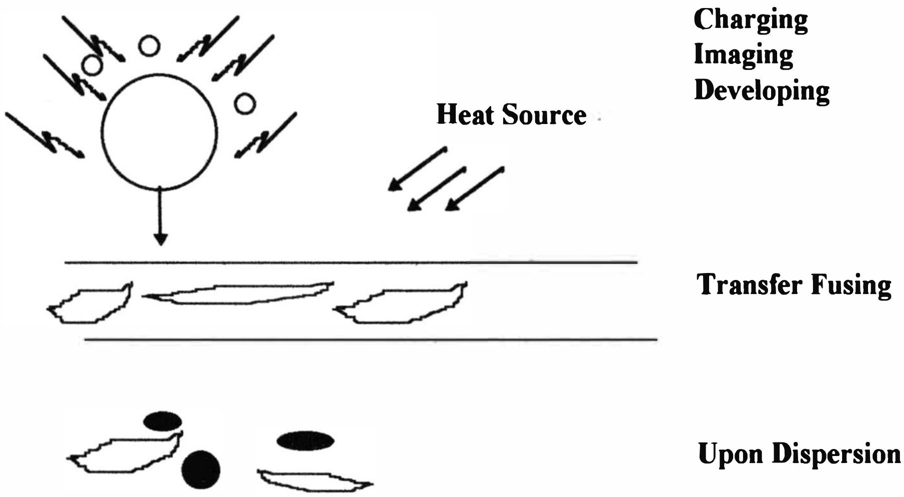
Flexographic and Xerographic inks are two of the most common inks used today. The most important component in determining the ease of ink removal is the ink vehicle. In flexographic inks, the vehicle consists of a resin to provide binding and a water solvent to provide fluidity. Flexographic inks are water-soluble inks which are naturally hydrophilic. Flexo ink resins, such as styrene acrylic, are based in acrylic resins which have the tendency to become water soluble and possibly dispersible when neutralized with organic bases. Flexographic inks also contain latex, which provide water resistance properties and fast drying times.[1]

Xerographic inks have been a concern of the paper industry for some time. The difficulty in removing this ink type is that it is made up of a plastic which has been bonded strongly to the fiber via heat (figure 1). Xerography is a dry method of reproduction, by which an image is produced in the form of electrostatic charges by reflecting the image onto the surface of a charged photoconductor, which holds its charges in the dark but not in the light. The photoconductor image is developed by contact with an ink powder (toner). This image is then transferred to the paper and fused via heat.[2]

This process results in large, flat shaped, fused ink particles that prove difficult to remove through screening and flotation. The size of these toner particles range from 40 to 400 μm. This is a concern due to the fact that flotation cells have been proved effective only when the particle sizes range from 30 to 150 μm. Therefore, proper alteration of the Xerographic ink particle and proper surfactant use are desired if they are to be removed efficiently in a flotation deinking system.[2,3]

Figure 1. Xerographic Method of Ink Adhesion to Fiber

- **Xerox**
- **Nonvehicle Ink**
- **Formation of specks**



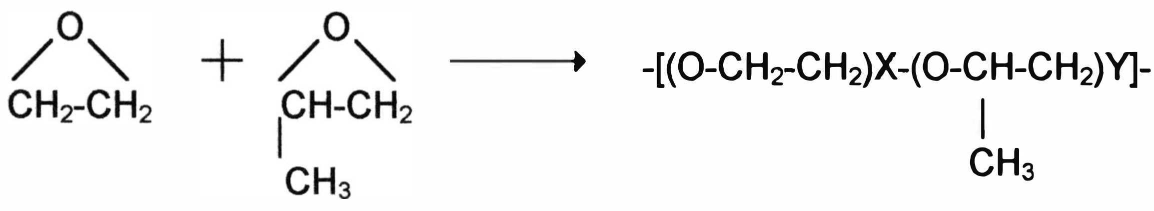
The primary problem in deinking lies in the toner-binder removal. To be successful, the resultant recycled furnish must be able to use the fiber in producing quality tissue grades or to a lesser extent, fine writing papers. In the past there have been two primary approaches in ink removal; mechanical dispersion and removal combination methods and chemical agglomeration removal methods. This experiment dealt with the agglomeration process of using flotation deinking and surfactants to remove ink particles.

Surfactants and the HLB Concept

Surfactants alter the surface tension between particles and it's medium. When a surfactant is added to a system, it causes an increase in the free energy of the system, causing the particle in question to rise to the interface at a lower work level. Surfactants can be further classified by their hydrophilic-lipophilic balance or HLB factor. This is the ratio of hydrophiles to lipophiles in that surfactant and it empirically determines the dispersive, emulsive, wetting, or solubulizing integrity of the surfactant. Hydrophiles are the part of the surfactant molecule that has a strong attraction for water. They may be large and consist of chains such as ethoxy groups. The lipophile part of the surfactant has very little affinity for water and consist of mainly carbon and hydrogen atoms.

As stated earlier, the contribution made by each of the previous mentioned parts of a surfactant can represented by an HLB value. Low HLB values correlate to a low polarity and low water solubility of the surfactant, and thus, a more hydrophobic surfactant. By contrast, a high HLB value means that the surfactant has high water solubility and high polarity. The most common surfactants used in deinking are surfactants that contain polymers of ethylene oxide/propylene oxide (EO/PO) copolymers. EO is the hydrophilic end and contains a high oxygen ratio, whereas PO is the hydrophobic end resulting from steric resistance from the extra methyl group (see figure 2).[2]

Figure 2. Ethylene Oxide/Propylene Oxide Copolymers



EO PO

In this experiment, a series of nonionic, anionic, and cationic surfactants were used. Nonionic surfactants do not ionize in water and have their solubility determined by polar groups. Nonionic surfactants have an advantage in that their individual efficiency is independent of pH and water hardness. Their efficiency has been shown to be dependent on HLB value, pH conditions, and critical micelle concentration (CMC). Cationic surfactants have an opposite charge to that of the electrostaticly negative charge of the ink particle and their effectiveness is a function of those charge groups. Anionic surfactant efficiency is primarily dependent on the pH conditions and the amount of hardening constituents present during flotation.[2,4]

Critical micelle concentration is the concentration at which micelles agglomerate in the flotation and cause no further decrease in reduction of surface tension. This a concern for surfactants in that proper ink removal through foaming does not occur until the CMC point is reached. Therefore, in an industrial setting, it is vital that the surfactant with the lowest possible CMC be used so that cost savings may be achieved. The following figure depicts CMC concentrations for various surfactant entities. Note that for nonionic surfactants the CMC values are almost two orders greater than those of the cationic variety. Research has shown that cationic surfactants have been known to show foaming at levels below the CMC.[1,4]

Figure 3. CMC Values for Various Surfactant Types

Surfactant Type	*Temperature (℃)*	*Critical Micelle Concentration (Molar)*
linear nonionic	25	4E-5
linear nonionic	25	5.5E-4
linear nonionic	25	8E-5
linear anionic	25	8.2E-3
linear nonionic	55	1.7E-5
linear anionic	50	1.3E-3
linear anionic	60	1.2E-3
linear cationic	25	1.6E-2
linear amphoteric	27	1.3E-3
linear nonionic	25	5E-5
linear nonionic	25	1.7E-6

Flotation Deinking Mechanisms

The use of flotation is mainly focused on removing larger particles rather than smaller particles when compared to washing deinking. This can be misleading due to the fact that flotation deinking is optimum only in particle size ranges of 30-150 microns. The primary difference between washing and flotation is the surface chemistry involved. In washing, the ink particles are rendered hydrophilic so that they may be removed with the water shower. In flotation deinking, the particle is initially also rendered hydrophilic, however, due to surfactant and collector interaction, the ink particle is rendered hydrophobic and subsequently removed via air bubbles.[5]

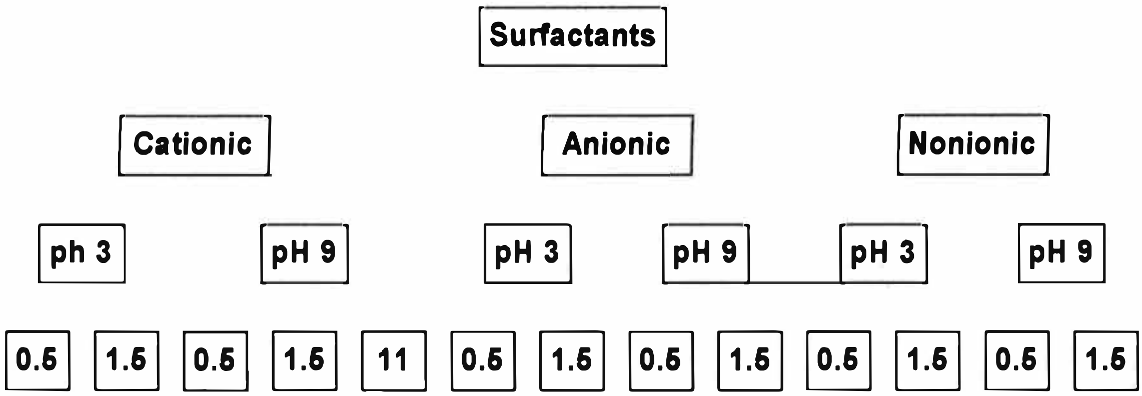
The mechanism of removal for ink particles involves reactions of ink micelle formation and air bubble interaction. After the saponification of an ink particle, positively charged calcium ions (from the water or surfactant agglomerate) react with the negatively charged ink surface. This reaction neutralizes the charges on the micelles surrounding the ink surface causing hydrophobicity. When enough surfactant is present (CMC), the particle-micelle agglomerate may now be deposited onto air bubbles for froth removal. Important parameters for flotation optimization are bubble size, surfactant integrity, ink particle type, pH, temperature, and water hardness.[5]

Experimental Procedure

This experiment was divided into the following sections: selection of the surfactant series, preparing the ink and paper substrate, evaluating the series of surfactants on the ink-paper substrate via flotation, evaluating the ink removal efficiency accordingly, and finally correlating the removal efficiency to the corresponding surfactant, structure, and HLB number.

Initially, the three series of surfactants were chosen based on availability and precision of the HLB values. The following diagram details the experimental design.

Figure 4. Experimental Procedure



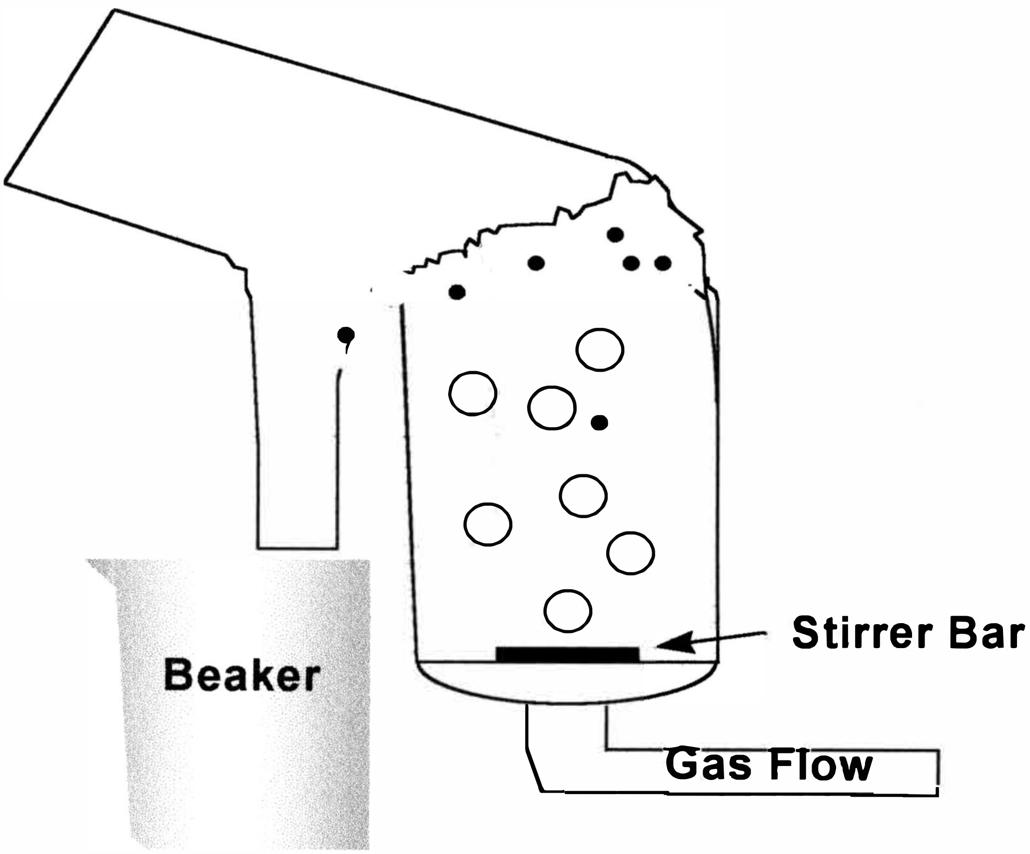
Pulp Preparation

The entire process consisted of a re-pulping stage and flotation stage. The samples were printed using Xerox toner, a negatively charged toner, and a Hammermill paper substrate . Initially, 25 grams of Xerographically printed copy paper was mixed with reverse osmosis water to make a 2 Liter suspension. The mixture was re-pulped via disintegration for 50,000 revolutions. Then, 100 mL of this pulp was diluted with 1 Liter of reverse osmosis water to achieve a 0.1% slurry. This is the recommended consistency for use of the Hallimond Tube.

Flotation and Surfactant Use

The surfactants were applied at concentrations of 0.5%, 1.5%, and 11% respectively for each type, based on oven dry fiber. Nonionic surfactants were supplied by Shell Corporation. The cationic and anionic surfactants were supplied by Witco Corporation. The flotation occurred in a Hallimond Tube (see figure 5). The Hallimond Tube is a laboratory scale flotation apparatus made from manipulated Pyrex. It has the capacity to float 90 mL of fluid. The slurry was floated with in the tube with a magnetic stirrer to achieve uniform bubble size.

Figure 5. Hallimond Tube



Runs were performed at each surfactant addition level and pH condition twice for average calculation. Note that the 11% surfactant addition was used to see the effects of tremendous foaming. This was done because minimal foaming was seen initially in some runs. Control runs, without surfactant addition, were also performed to calculate efficiency. Image analysis was performed on each furnish after the process and compared to the control value. These results were calculated to determine efficiency ratings.

Results and Discussion

The results for this experiment were achieved through the use of image analysis software. The software, SpecScan 2000, scans the sample pads via a Hewlett-Packard Scanner and prints out ink particle distribution and the number of specks for the desired area. From these results, flotation efficiency can be reported through the formula located in the appendices. In this experiment, hydrogen ion concentration, surfactant type, and surfactant dosage, were varied. Surfactant types were chosen as to their precision of HLB values so that conclusions could be correlated to predicted emulsification behavior.

Nonionic Surfactant Efficiency

Six types of nonionic alcohol ethoxylate surfactants were used. These surfactants had HLB values in the range of 6.3 to 14.5. The following figures show the results of ink removal efficiency for the nonionic series at acidic conditions.

Figure 6.

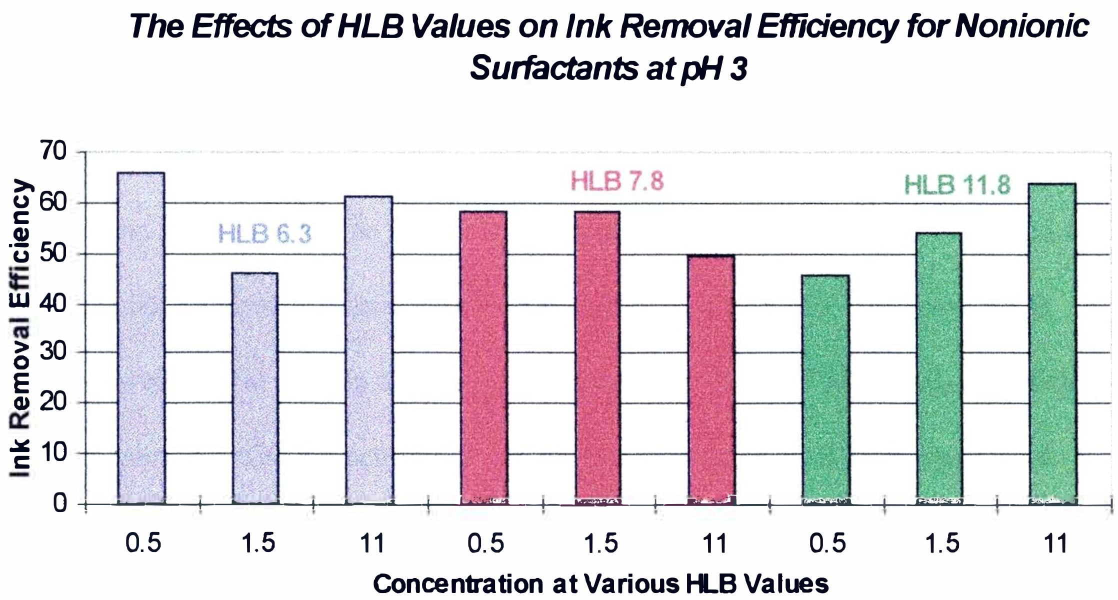
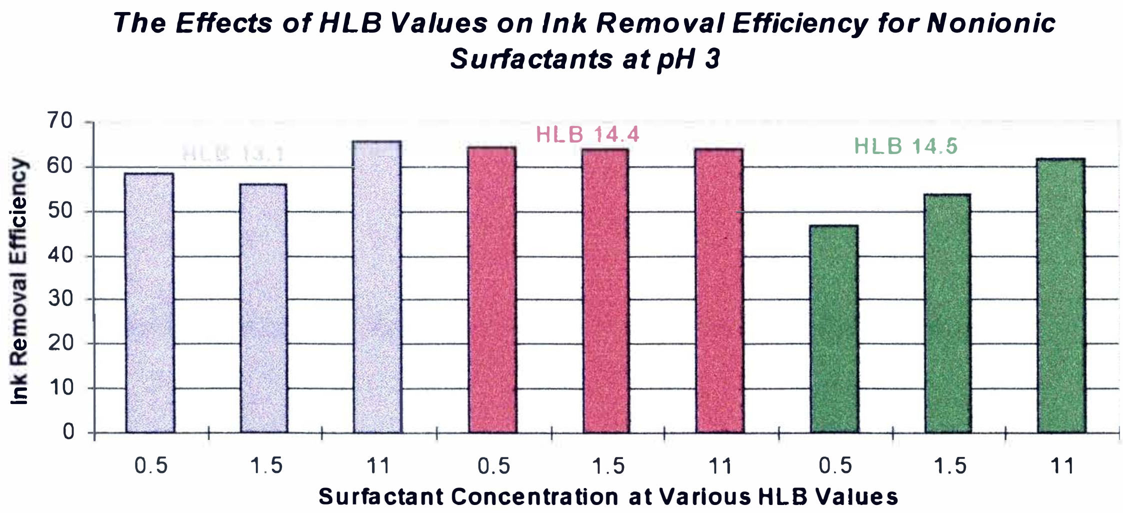


Figure 7.



It is important to note that the 11% concentration of surfactant was used to because foaming was minimal for various runs for all the surfactants tested. This percentage was used to achieve tremendous foaming and was then evaluated against yield later in this report. In application, however, surfactants are commonly used at concentrations of 0.5% to 3.0% (based on O.D. fiber). These surfactants were all tested above their CMC point.

From figure 6, it can be seen that the surfactant with an HLB of 11.8 resulted in a increase in ink removal efficiency with an increase in concentration. The lower HLB values showed no real relation to ink removal efficiency. As HLB increased, the efficiency increased generally with concentration. It can be seen that as HLB increased the ink removal efficiency increased form the general range of 50-60% to 60-70%.

Overall, the surfactants with the lower HLB gave inadequate to poor results. This is consistent with the literature and the manufacturers data. Surfactants of this type at these low HLB values are primarily water-in-oil emulsifiers and wetting agents. When used alone in a removal environment, they disperse poorly and give poor results.

The following figures show the results of same surfactants that were used under basic conditions.

Figure 8.

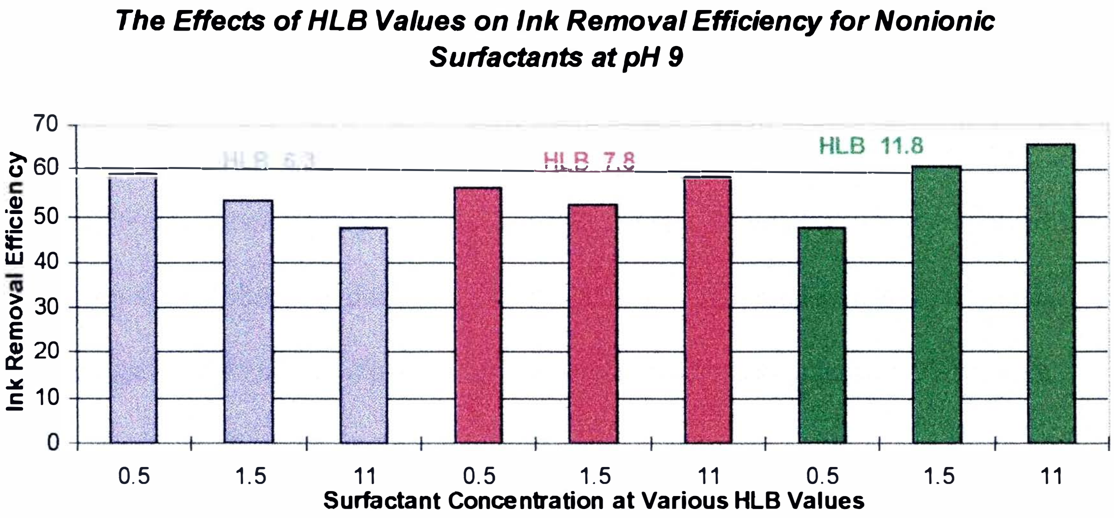
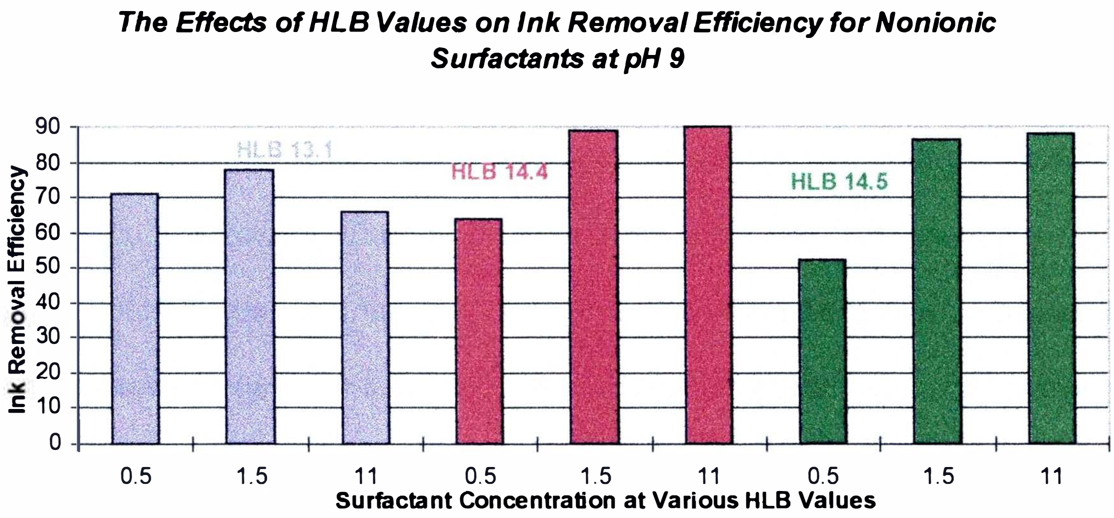


Figure 9.



Figures 8 and 9 show an overall increase of about 20% to 30% in ink removal efficiency when compared to figures 6 and 7. Again, the trend of increasing concentration and efficiency can be seen during basic conditions, but the magnitude is greater. Notice, that at the higher HLB levels, a more pronounced linear trend is seen than during acidic conditions. As the particles increase in hydrophilicity, the higher concentrations cause the attraction of the ink agglomerate to other micelles, rendering it hydrophobic. This increase in efficiency can also be attributed to high collection groups on the surfactant.

The increase in ink removal efficiency at pH 9 can be attributed to the swelling of the fibers by the caustic conditions. This swelling causes the ink particles to be lifted off them easier during shear conditions. Also, the higher pH conditions tend to break the ester linkages in the ink particle, causing it to break into smaller particles. This is also consistent with applications and the literature.

Thus, for the nonionic surfactants, higher HLB values gave higher ink removal efficiencies. The surfactants with HLB values of 14.4. and 14.5 gave results of 80% and 90% efficiency during basic conditions. Overall, the surfactants performed better at pH 9.

Cationic Surfactant Efficiency

The cationic surfactants used in this experiment were dialkyl dimethyl quaternary compounds. The results of three surfactants were chosen for analysis due to their precision of HLB values with the other surfactants. Their general structure is a positively charged quaternary base with a chloride or methyl sulfate attached. Due to their charge, they readily attract the negatively charged ink particle. The following figures show the results of ink removal efficiency for the cationic surfactants at pH 3 and pH 9 respectively.

Figure 10.

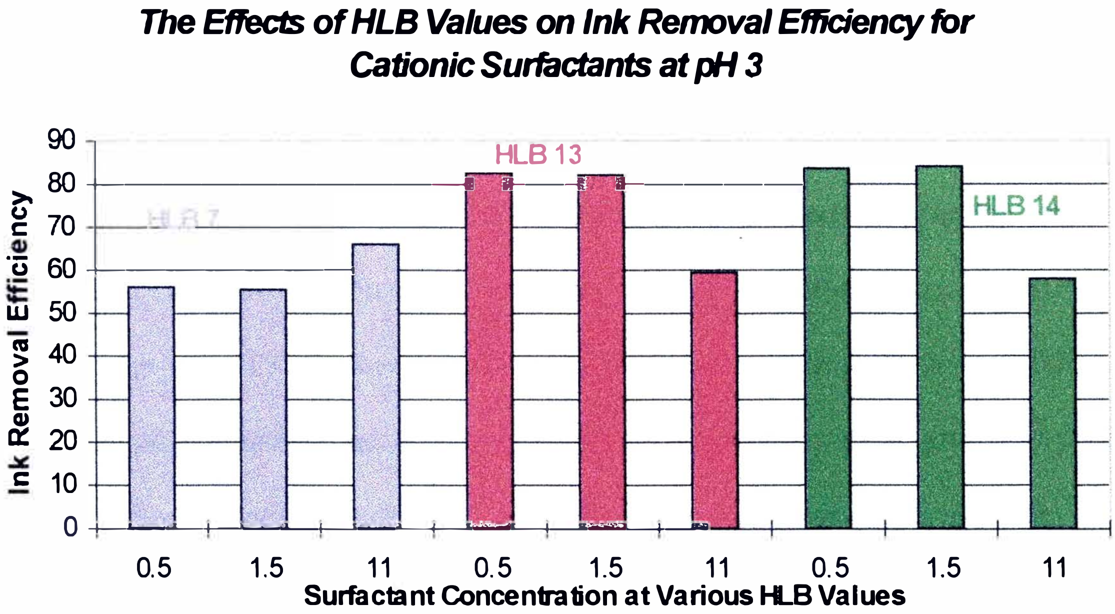
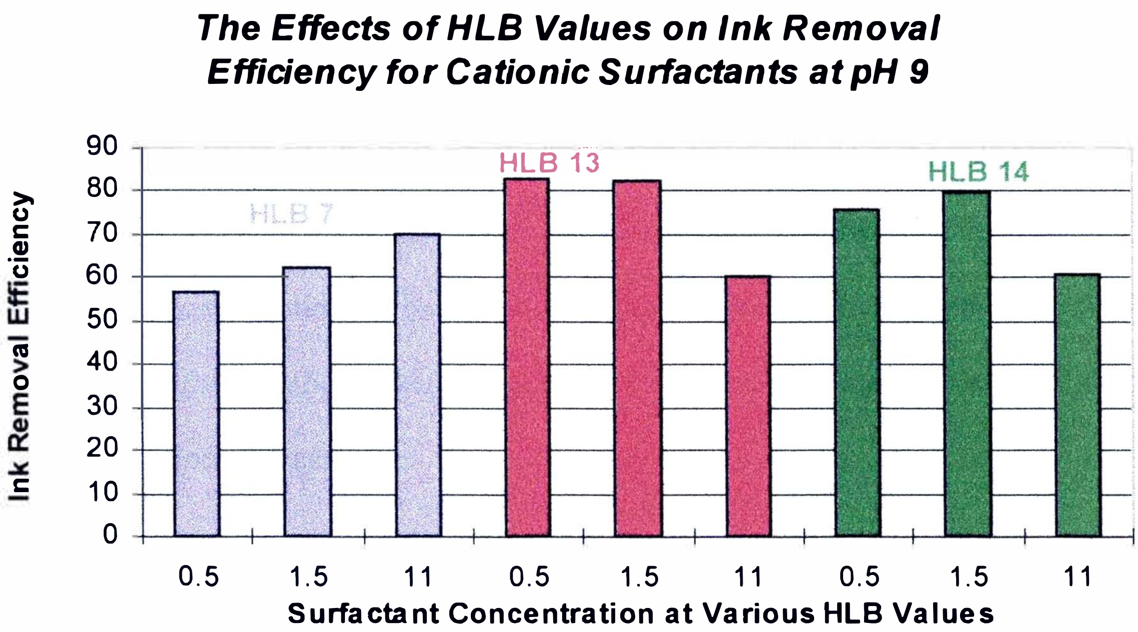


Figure 11.



The cationic surfactants shown in figures 10 and 11 resulted in high efficiencies. For the acidic conditions, the lower HLB valued surfactant resulted in poor efficiencies of 55% to 65% ink removal. However, the surfactants with HLB values of 13 and 14 resulted with similar efficiencies of 82% to 85% respectively.

The change in pH conditions resulted in little deviance of efficiency for the cationic surfactants. This can be attributed to the lowering of the natural fiber charge to zero as pH decreases. At pH 3, the fiber charge is zero, this aids the surfactant by lowering the work required to release the ink particles. Thus, the surfactant can attract and remove the negatively charged particle much easier, but showing similar efficiency ratings to that of the pH 9 conditions.

Anionic Surfactant Efficiency

The anionic surfactants used in this study gave poor results. The surfactants that were correlated were of the primary structure, sodium dodecylbenzenesulfonate. All results seemed to show no real correlation. In addition, pH and HLB seemed to have little or no effect. The inherently negative charge of the anionic surfactants could also have repelled themselves from the negatively charged ink particles. The following figures show the results obtained. Notice that only three surfactants were charted. This was due to the lack of HLB information by the manufacturer, and the fact that other tested data resulted in poor, non-trending results.

Figure 12.

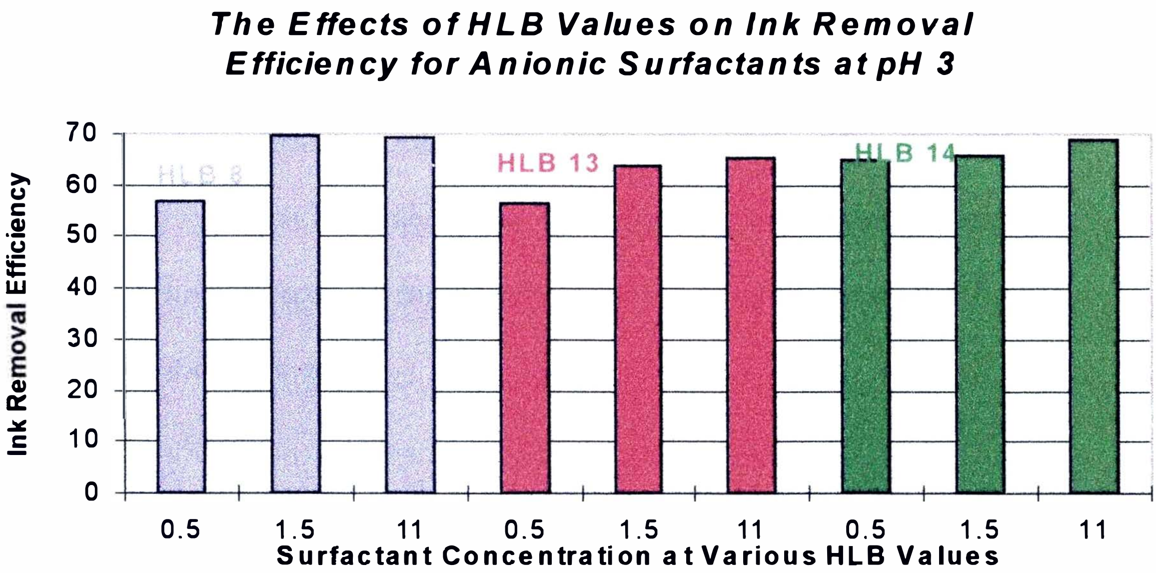
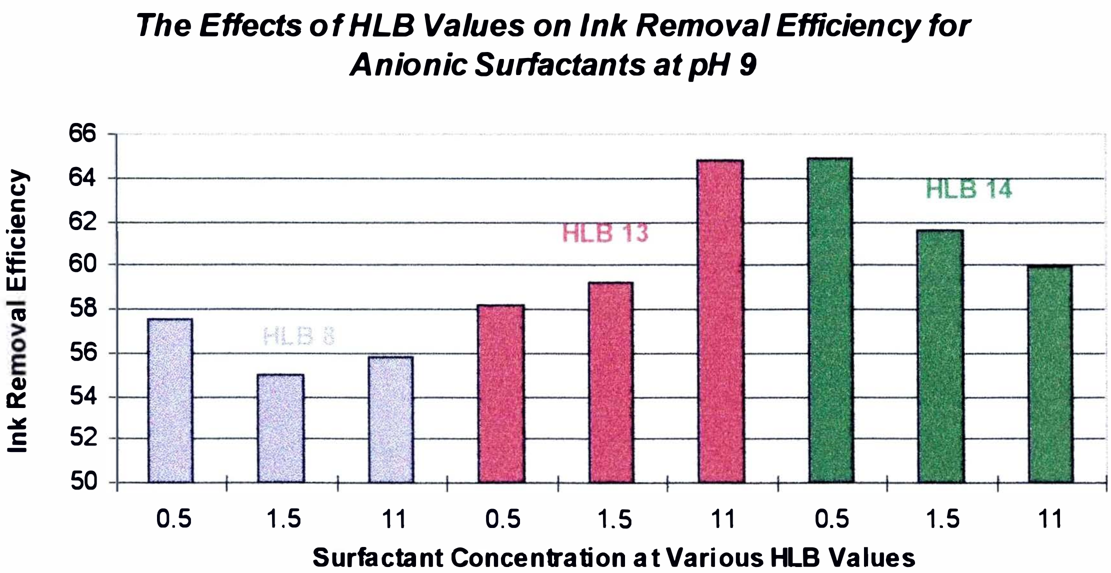


Figure 13.



As figures 12 and 13 depict, no positive trend exists for the anionic surfactants. There is an increase in efficiency for the surfactant at high HLB values, during pH 9, however, these efficiencies are very poor. This increase can be attributed to fiber swelling and release of the ink particle. Literature has shown that anionic surfactants of this type are resistant to hydrolysis in hot acid or alkali, and that they are commonly ionized completely in water without any solubilization effects at low pH.[6] These are believed to the causes for such poor results.

Conclusions

1. An increase in surfactant concentration increased ink removal efficiency for the nonionic, and cationic surfactants. The anionic surfactants showed a slight increase in efficiency, but only at the high HLB values. Overall, the nonionic and cationic surfactants had the best ink removal efficiency. Of these surfactants, an increase in ink removal efficiency correlated to a net increase in HLB.
2. The cationic surfactants resulted in higher overall ink removal efficiencies. Efficiencies of 82% to 85% and 80% to 83% were observed at pH 3 and pH 9 respectively. For the acidic conditions, the lower HLB valued surfactant resulted in poor efficiencies of 55% to 65% ink removal. However, the surfactants with HLB values of 13 and 14 resulted with similar efficiencies of 82% to 85% respectively.
3. For the nonionic surfactants, higher HLB values gave higher ink removal efficiencies. The surfactants with HLB values of 14.4. and 14.5 gave results of 80% and 90% efficiency during basic conditions. Overall, the nonionic surfactants performed better at pH 9.
4. Alkaline conditions showed better results for the nonionic than cationic. Higher pH levels promote the swelling of fibers to subsequently release the ink particles. Also, the higher pH conditions tend to break the ester linkages in the ink particle, causing it to break into smaller particles.

Recommendations for Further Study

This introductory research has shown promise for optimizing surfactant selection based on HLB and ink removal efficiency correlation's. This experiment studied the three main commercial types of surfactants used in industry to establish such a need for further research. Further research is recommended in the areas of temperature effects, higher consistency ranges, and toner types. The process of using surfactants with known structures and adding collection groups and charge groups to study the groups effects on a microscopic level is also suggested.

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Appendices

Ink Removal Efficiency Data
Particle Counts and Effciencies

Surfactant Type	*HLB Value*	*pH*	*Concentration % on O.D. Fiber*	*Ink Removal Efficiency %*	*Ink Particle Count*	*Count w/o Surfactant*
Cationic	7	3	0.5	55.85	728	1649
Cationic	7	9	0.5	56.52	717	1649
Cationic	7	3	1.5	55.37	736	1649
Cationic	7	9	1.5	61.98	627	1649
Cationic	7	3	11	65.98	561	1649
Cationic	7	9	11	70.10	493	1649
Cationic	13	3	0.5	82.47	289	1649
Cationic	13	9	0.5	82.60	287	1649
Cationic	13	3	1.5	81.81	300	1649
Cationic	13	9	1.5	82.05	296	1649
Cationic	13	3	11	59.73	664	1649
Cationic	13	9	11	59.92	661	1649
Cationic	14	3	0.5	83.26	276	1649
Cationic	14	9	0.5	75.80	399	1649
Cationic	14	3	1.5	83.99	264	1649
Cationic	14	9	1.5	79.50	338	1649
Cationic	14	3	11	58.22	689	1649
Cationic	14	9	11	60.70	648	1649
Anionic	8	3	0.5	56.82	712	1649
Anionic	8	9	0.5	57.55	700	1649
Anionic	8	3	1.5	69.80	498	1649
Anionic	8	9	1.5	55.00	742	1649
Anionic	8	3	11	69.25	507	1649
Anionic	8	9	11	55.79	729	1649
Anionic	13	3	0.5	56.52	717	1649
Anionic	13	9	0.5	58.22	689	1649
Anionic	13	3	1.5	63.80	597	1649
Anionic	13	9	1.5	59.19	673	1649
Anionic	13	3	11	65.25	573	1649
Anionic	13	9	11	64.77	581	1649
Anionic	14	3	0.5	64.95	578	1649
Anionic	14	9	0.5	64.89	579	1649
Anionic	14	3	1.5	65.62	567	1649
Anionic	14	9	1.5	61.61	633	1649
Anionic	14	3	11	68.95	512	1649

Ink Removal Efficiency Data
Particle Counts and Effciencies

Surfactant Type	HLB Value	pH	Concentration % on O.D. Fiber	Ink Removal Efficiency %	Ink Particle Count	Count w/o Surfactant
Anionic	14	9	11	59.92	661	1649
Nonionic	6.3	3	0.5	65.80	564	1649
Nonionic	6.3	9	0.5	58.88	678	1649
Nonionic	6.3	3	1.5	45.97	891	1649
Nonionic	6.3	9	1.5	53.37	769	1649
Nonionic	6.3	3	11	61.13	641	1649
Nonionic	6.3	9	11	47.42	867	1649
Nonionic	7.8	3	0.5	58.22	689	1649
Nonionic	7.8	9	0.5	56.16	723	1649
Nonionic	7.8	3	1.5	58.22	689	1649
Nonionic	7.8	9	1.5	52.58	782	1649
Nonionic	7.8	3	11	49.61	831	1649
Nonionic	7.8	9	11	58.88	678	1649
Nonionic	11.8	3	0.5	45.60	897	1649
Nonionic	11.8	9	0.5	47.60	864	1649
Nonionic	11.8	3	1.5	54.28	754	1649
Nonionic	11.8	9	1.5	61.07	642	1649
Nonionic	11.8	3	11	63.67	599	1649
Nonionic	11.8	9	11	65.62	567	1649
Nonionic	13.1	3	0.5	58.22	689	1649
Nonionic	13.1	9	0.5	70.95	479	1649
Nonionic	13.1	3	1.5	55.79	729	1649
Nonionic	13.1	9	1.5	77.62	369	1649
Nonionic	13.1	3	11	65.49	569	1649
Nonionic	13.1	9	11	65.80	564	1649
Nonionic	14.4	3	0.5	64.40	587	1649
Nonionic	14.4	9	0.5	64.04	593	1649
Nonionic	14.4	3	1.5	64.04	593	1649
Nonionic	14.4	9	1.5	88.90	183	1649
Nonionic	14.4	3	11	63.80	597	1649
Nonionic	14.4	9	11	89.87	167	1649
Nonionic	14.5	3	0.5	46.69	879	1649
Nonionic	14.5	9	0.5	52.15	789	1649
Nonionic	14.5	3	1.5	53.67	764	1649
Nonionic	14.5	9	1.5	86.60	221	1649

Ink Removal Efficiency Data
Particle Counts and Effciencies

Surfactant Type	HLB Value	pH	Concentration % on O.D. Fiber	Ink Removal Efficiency %	Ink Particle Count	Count w/o Surfactant
Nonionic	14.5	3	11	61.61	633	1649
Nonionic	14.5	9	11	88.05	197	1649
Control						1649